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EFFECTS OF GASES ON PHOTOIONIZATION OF CÆSIUM BY LINE ABSORPTION

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ABSTRACT

Relative measurements of the photoionization by line absorption in cæsium vapor with and without foreign gases were made by the space-charge method. If the effect of a collision with a gas molecule is to change the probability of ionization from E_o to E_f, then the probability E_p at a gas pressure p is given by

$$\frac{E_o}{E_o-E_p}=\frac{E_o}{E_o-E_f}\left(1+\frac{1}{A\sigma^2\tau' p}\right)$$

where A is a known constant, σ is the distance between atom centers at collision and τ' is the life of the excited state.

Nitrogen reduces the ionization of states 4 P to 8 P by about the same amounts. $\sigma^2\tau'$ is of the order of 10^{-21} cm^2 sec. and $E_f/E_o=0.1$. Hydrogen gives about the same result. Helium increases the ionization of 4 P (E_f/E_o for 4 P_1 is 3) and decreases the effect of other lines to 60 or 70 per cent at high pressure. $\sigma^2\tau'$ is 10^{-21} for 5 P and less for other states. Argon gives very little effect. The effectiveness of nitrogen increases about threefold when the cæsium pressure is changed from 0.012 to 0.002 mm, and the computed change in τ' accounts for this variation. Results indicate a value of σ between 1.4 and 4×10^{-8} for all foreign gases, while the value for the Cs-Cs collision giving ionization was ten times this.

CONTENTS

	Page
I. Theory	399
II. Procedure	401
III. Experimental results	402
1. Nitrogen	402
2. Helium	404
3. Hydrogen	405
4. Argon	406
5. Effect of nitrogen as a function of cæsium pressure	406
IV. Discussion	406

I. THEORY

Another paper by the authors [1] describes experiments on the photoelectric ionization of cæsium vapor by radiation of wave length longer than the absorption series limit. The results indicate that this ionization involves the production of an excited atom by line absorption and the subsequent collision of the excited atom and a normal atom. This supports a theory suggested by Franck that ionization results from the combination of an excited atom and a normal atom to form a molecule ion.

This paper reports experiments on the modifications of this ionization which are produced when foreign gases are added to the cæsium. The results can be understood without any assumptions as to the

[1] Mohler and Boeckner, B. S. Jour. Research, 5 (RP186), p. 51; July, 1930.

mechanism of the ionization process except that excited atoms collide with normal cæsium atoms and are ionized with a probability which depends on the state of excitation. The collisions with other atoms will change the state of excitation and modify the probability of ionization.

The ionization process is itself a collision process, and a brief recapitulation of the theory and results presented in the first paper will be given here. Experimental data were reduced to values of the probability E of ionization of the different excited states expressed as a function of the cæsium pressure. The probability of a collision during the lifetime of an excited state [2] is

$$P=\frac{\tau}{T+\tau} \tag{1}$$

where T is the mean time between collisions and τ the mean life of the excited state. For the general case of two gases of molecular weights m_1 and m_2

$$T=\frac{1}{A\,\sigma^2 p},\quad A=2.0\times 10^{22}\sqrt{\frac{m_1+m_2}{m_1\,m_2}},$$

$$\frac{1}{P}=1+\frac{1}{A\,\sigma^2\,\tau\,p} \tag{2}$$

where p is the pressure in millimeters of mercury and σ is the distance of approach of the two atoms at collision. The constant is evaluated for a working temperature of 500° K.

We assume that the probability of ionization E at a pressure p is equal to the probability of ionization at a collision, E_c, times the probability of a collision during the life of the excited state

$$E=E_c\,P$$

$$\frac{1}{E}=\frac{1}{E_c}\left(1+\frac{1}{A\,\sigma^2\,\tau\,p}\right) \tag{3}$$

Plots of reciprocals of E and p gave straight lines and Table 1 repeats the numerical values of E_c and $\sigma^2\tau$ derived from these lines. Collisions with cæsium atoms modify the lives of the excited states. If we assume that each collision destroys the excited state, then the actual life τ' is given by

$$\frac{1}{\tau'}=\frac{1}{\tau}+\frac{1}{T} \tag{4}$$

At the pressure for which $E=\frac{1}{2}E_c$, $\tau=T$ and $\tau'=\frac{1}{2}T$.

For states 5 P to 8 P the half value is reached at nearly the same pressure 0.0038 mm, and from this one can compute the ratio of τ' to τ for any cæsium pressure.

$$\frac{\tau}{\tau'}=1+\frac{p}{0.0038} \tag{5}$$

[2] Turner, Phys. Rev., 23, p. 464; 1924.

TABLE 1.—*Constants for cæsium-cæsium collisions* [1]

m	1S−mP	E_o	$\sigma^2\tau$	p in mm for $E/E_o=\frac{1}{2}$
4	3,888	0.003	0.22×10^{-19}	0.02
5	3,612	.154	1.0×10^{-19}	.0042
6	3,477	.26	1.1×10^{-19}	.0032
7	3,398	.40	1.1×10^{-19}	.0042
8	3,347	.50	1.0×10^{-19}	.0038
9, 10	3,300	.77	1.2×10^{-19}	.0032
12, 13	3,250	.89	3.3×10^{-19}	.0011
16	3,225	.93	16×10^{-19}	.0002
25	3,200	1.0	48×10^{-19}	.00007

[1] Mohler and Boeckner, B. S. Jour. Research, 5 (RP186); July, 1930.

The collision of an excited atom with a foreign gas will change the probability of ionization, and the simplest case is when the collision reduces the probability to zero. Then, if E_o is the probability of ionization in pure cæsium vapor at a fixed vapor pressure and E_p the probability of ionization with a foreign gas at a partial pressure, p, the probability of collision of an excited atom with the foreign gas is

$$P=\frac{E_o-E_p}{E_o}$$

More generally the collision will change the probability of ionization from E_o to E_f and

$$P=\frac{E_o-E_p}{E_o-E_f}=\frac{E_o-E_p}{E_o}\frac{E_o}{E_o-E_f}$$

equation (2) becomes

$$\frac{E_o}{E_o-E_p}=\frac{E_o}{E_o-E_f}\left(1+\frac{1}{A\sigma^2\tau' p}\right) \tag{6}$$

II. PROCEDURE

We use as before the neutralizing effect of positive ions on a thermionic current limited by negative space charge to measure the photoionization. Curves of photoionization as a function of wave length are obtained in pure cæsium and in cæsium with a foreign gas. The gas reduces the amplification factor of the space-charge tube by an unknown amount, but we can safely assume that the presence of gas does not change the number of ions produced by direct ionization by wave lengths shorter than the series limit (3,184). If the two curves are reduced to the same scale of ordinates at and beyond the limit, then the ratio of ordinates at any wave length in the region of line absorption measures the effect of the foreign gas on the process of ionization. If the line absorption is not changed by the gas, this ratio of ordinates is E_p/E_o, the ratio of probabilities of ionization of an excited atom with and without the gas present. Absorption lines are broadened by foreign gas, but by an amount that can be neglected for the low pressures here used.[3]

[3] Füchtbauer and Hoffman, Ann. der Phys., 43, p. 96, 1914, give the broadening of cæsium lines by nitrogen as 0.3 *A* at 2,360 mm, or 0.00013 *A* per mm.

To improve precision we have used a refinement of the space-charge method developed by Lawrence and Edlefsen[4] in most of this work. Instead of balancing the dark current in a 2-electrode tube, they use two cylindrical anodes around a single axial cathode. Light is admitted to one chamber and the resulting difference in current to the two anodes is measured. This automatically compensates for small fluctuations. We have followed the general scheme of tube design and electrical circuits described by Lawrence and Edlefsen except that illumination was through a slit in the side of one cylinder.

The tubing connecting the ionization chamber to the pumps had a 2 cm section of 1 mm capillary tubing at about 15 cm from the chamber, and the cæsium was kept on the chamber side of the capillary and maintained by a separate heater at the temperature which determined the vapor pressure. Liquid cæsium quickly collected in the constriction and sealed it, preventing rapid loss into the pump system. Application of a flame opened the chamber to the rest of the system whenever it was desired. A mercury cut-off on the pump side of a liquid air trap and McLeod gauge served to admit and trap the gas.

Light from a Mazda projection lamp, resolved by a Bausch & Lomb monochromator, was used for continuous spectrum illumination. Studies of the effect of the 3,888 helium line were made by direct comparison with the effect of the 3,130 mercury line. A mercury arc and a helium tube were arranged so that both illuminated the slit of the monochromator, and the comparison was made by changing the monochromator setting. In this case the space charge effect is very large and not proportional to the intensity; so, for each condition, the current intensity relation had to be determined. The helium line is coincident with 1 S−4 P_1 and gives excited atoms in the state 4 P_1. The continuous spectrum peak is the unresolved effect of 3,888 and 3,877 giving states 4 P_1 and 4 P_2, and the latter is probably predominant because it is more strongly absorbed.

It is to be expected that the effects of different gases are quite sensitive to impurities, but it is not feasible to obtain high purity by the usual technique of prolonged streaming or flushing out of the system without accumulating impurities in the cæsium. This is probably the chief source of experimental uncertainty.

III. EXPERIMENTAL RESULTS

1. NITROGEN

Figure 1 shows curves of photoionization versus wave length in pure cæsium at 0.005 mm, and in cæsium vapor with 0.143 mm of nitrogen and with 2.25 mm. The effect is to reduce ionization by line absorption at all lines on the red side of 3,200 A, and all resolved lines are reduced by about the same magnitude. The sensitivity of the space charge effect becomes very low for pressures greater than 2 or 3 mm of nitrogen. Experiments on the ionization produced by the 3,888 helium line gave results which were about the same as those obtained by continuous spectrum excitation; showing that the states 4 P_1 and 4 P_2 are modified by nitrogen in much the same way.

[4] Lawrence and Edlefsen, Phys. Rev., 34 p. 233; 1929.

From the ratio of ordinates, E_p/E_o, we derive $E_o/(E_o-E_p)$ and Figure 2 gives a plot of this function against $1/p$. Results are not accurate enough to prove that a linear relation exists, but straight lines fall well within the range of experimental error and permit an interpretation of results in terms of equation (6). From this equation we see that if the probability of ionization is reduced to zero at a collision the intercept at $1/p=0$ will be one. The intercept for the resolved lines, 3,349 to 3,888, is nearly one but definitely above, both

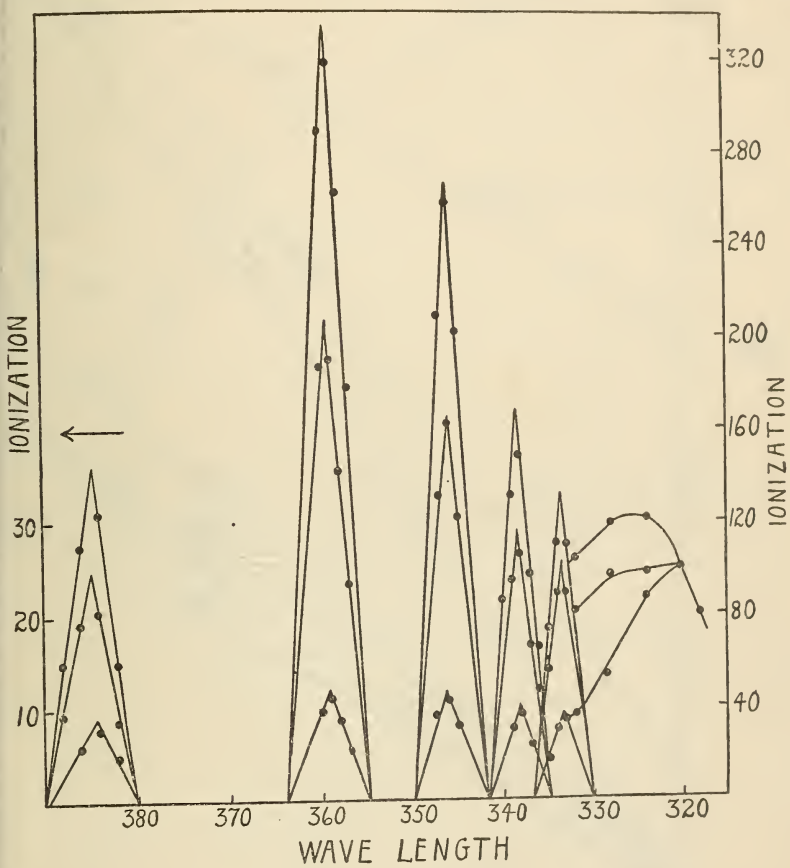

FIGURE 1.—*Ion current as a funtion of wave length*

The upper curve gives the effect in pure caesium, the middle curve with nitrogen at 0.143 mm, the lower curve with nitrogen at 2.25 mm.

in Figure 2 and in other similar runs. For settings near the limit, notably at 3,240, incomplete resolution may partially mask the pressure variation and the observed difference between 3,240 and other wave lengths is in the direction to be expected from this cause. Of course, in reciprocal plots the error becomes very great for large ordinates. The lines in Figure 2, unlike the reciprocal plots for ionization as a function of pressure, do not change progressively as we go to the higher states.

2. HELIUM

The effect of helium on photoionization is quite different from that of nitrogen. As it has a smaller effect on the space-charge effect, a wider pressure range could be studied. Figure 3 gives the relative

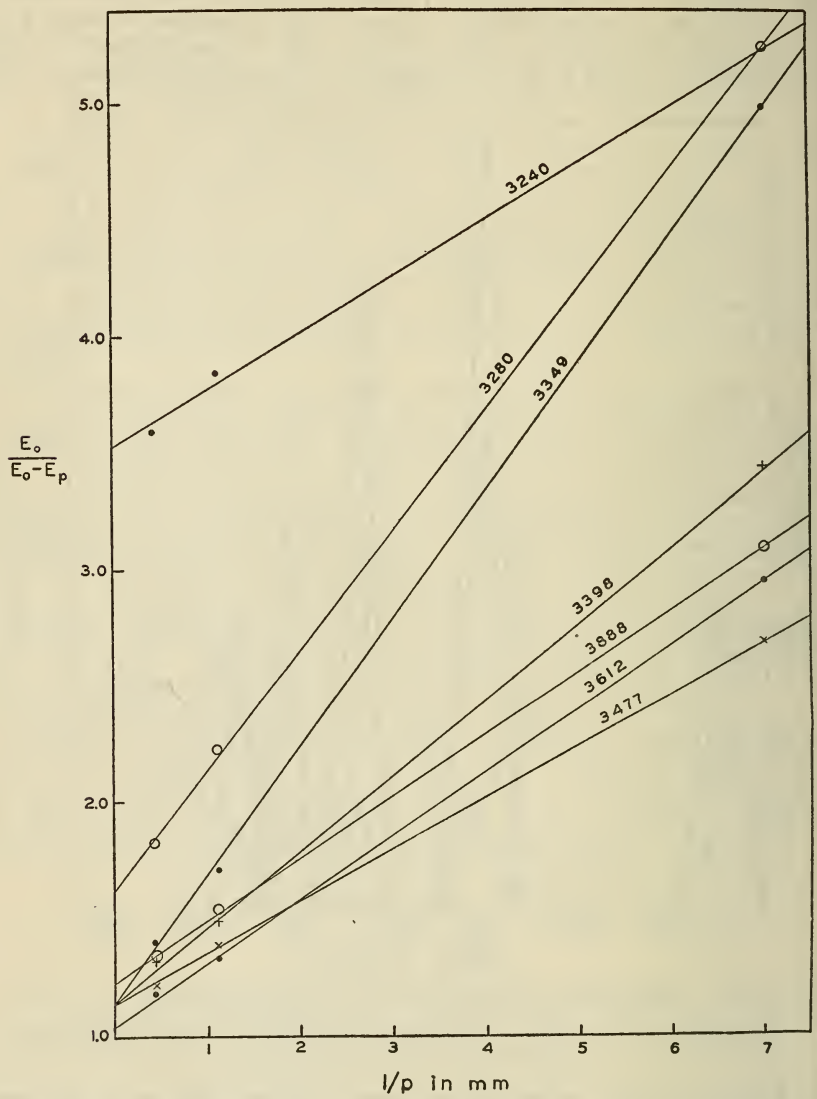

FIGURE 2.—*Plots of $E_o/(E_o-E_p)$ versus 1/p for the effect of nitrogen on cæsium ionization*

change in ionization, E_p/E_o, as a function of pressure. The ionization of states 4 P_1 and of 4 P_1 and 4 P_2 increases with the addition of helium and the increase is different for the two cases. The ionization of all other states is decreased somewhat, and apparently the probability has a minimum value at 2 or 3 mm and slowly increases for higher pressure.

Plots $E_o/(E_o-E_p)$ against $1/p$ are shown in Figure 4. The measurements at lower pressures give a basis for drawing the straight lines, but the observed increase at high pressures gives, of course, a large departure from the linear relation near $1/p=0$.

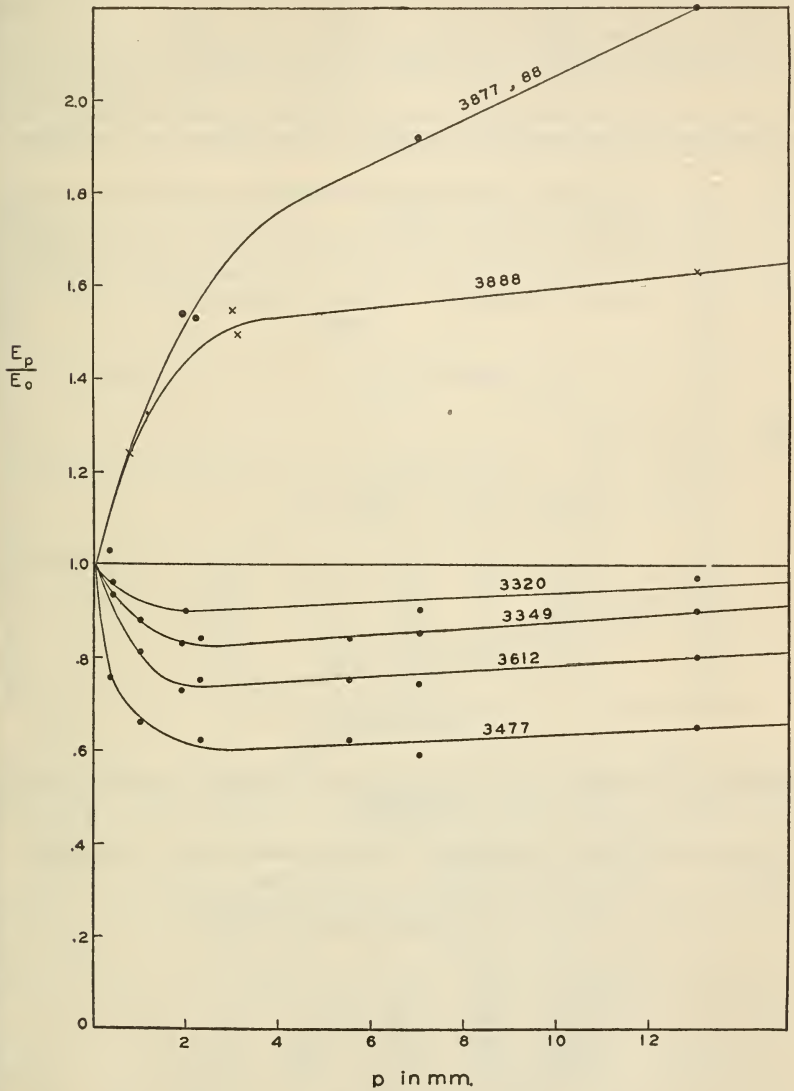

FIGURE 3.—E_p/E_o *as a function of pressure of helium*

3. HYDROGEN

Measurements with hydrogen are subject to experimental uncertainty because of reaction with the cæsium. After admission of hydrogen the pressure continuously drops, and prolonged pumping was required to again attain a vacuum. After several days of pump-

ing the tube was sealed off and the pressure again rose sufficiently to reduce sensitivity to line absorption to about 12 per cent of the vacuum value. The hydrogen must modify the cæsium partial pressure, but our method eliminates first-order errors from this cause. Small hydrogen pressures give a marked decrease in the ionization, and Table 2 gives results. A plot of $E_o/(E_o-E_p)$ against $1/p$ indicates that the best lines through observed points for states 5 P and 6 P have intercepts near one. For higher states data for measured pressures do not fall on lines through 1 at $1/p=0$ but the observed low efficiency at an unknown high pressure indicates that for these states too the intercept is nearly one and the other points are probably in error.

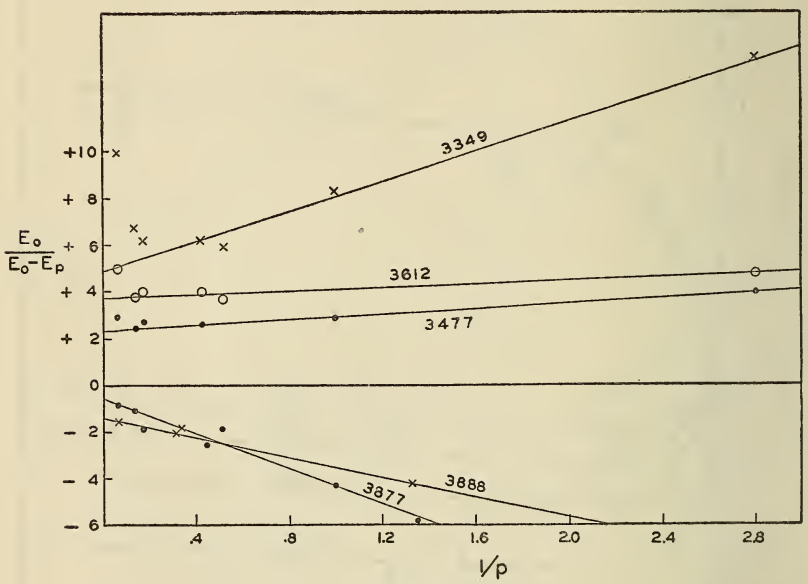

FIGURE 4.—*Plots of $E_o/(E_o-E_p)$ versus $1/p$ for the effect of helium on cæsium ionization*

TABLE 2.—*Ionization with hydrogen as compared with pure cæsium, E_p/E_o*

Line	0.02 mm	0.08 mm	0.15 mm	Unknown high pressure
3,877	0.77	0.59	----------	----------
3,612	.78	.52	0.36	0.12
3,477	.78	.52	.31	.14
3,398	.77	.68	.50	.12
3,347	.80	.78	.48	.15

Hydrogen is the most common impurity in alkali vapors, and the results show that it can be a serious source of error in any experiments involving the duration of excited states. These experiments were, in fact, initiated by the observation that hastily prepared ionization tubes gave an abnormally low sensitivity to line absorption. Carefully outgassed tubes seem to retain the full sensitivity, however, after sealing off.

4. ARGON

Argon gives a large reduction in space-charge effect and a small change in relative sensitivity. Successive runs showed discrepancies which suggest that impurities play an important part. The effect at 3,877 and 3,888 was increased roughly 20 per cent by the addition of argon. The peaks at 3,612 and 3,477 were reduced to about 60 per cent by 2.6 mm of argon and other lines less. Reciprocal plots of data at this and lower pressures indicate that the lines for states above 4 P have intercepts near 1 at $1/p=0$.

5. EFFECT OF NITROGEN AS A FUNCTION OF CÆSIUM PRESSURE

The above results apply to the effects of a foreign gas at a fixed cæsium pressure of 0.005 mm. A series of measurements on the effect of 0.134 mm of nitrogen at various cæsium pressures is given in Table 3. The results show a marked increase in the effectiveness of nitrogen with decreasing cæsium pressure though accidental variations are rather large.

TABLE 3.—*Effect of 0.134 mm of nitrogen at various cæsium pressures in terms of* E_p/E_o

Line	Cæsium pressures			
	0.0019	0.0028	0.0048	0.0126
3,877	----------	0.74	0.68	0.89
3,612	0.46	.48	.66	.68
3,477	.42	.52	.63	.73
3,398	.52	.50	.71	.79
3,349	.61	.62	.80	.85
3,320	.67	.60	----------	.87
3,280	.60	.68	.81	.95

IV. DISCUSSION

Other studies of the various effects produced when excited atoms collide with other atoms or molecules [5] indicate that in some cases the predominant effect is a transition from the excited state to the normal state; in other cases the most probable result is a change in the state of excitation involving a minimum dissipation of energy. Boeckner [6] has studied resonance radiation of cæsium excited by the 3,888 helium line in pure cæsium and in the presence of helium. In pure cæsium only those lines are emitted which result from permitted radiation transitions from 4 P_1. Helium collisions change the state of excitation to the neighboring states 4 P_2 and 5 D, which differ from 4 P_1 by 0.01 and 0.04 volt, respectively. Transitions by collision to other states which all differ from 4 P_1 by more than 0.14 volt are quite negligible. The effect of helium was to increase the ionization produced by 3,888. We know that in pure cæsium 4 P_2 is ionized with roughly the same probability as 4 P_1, so we conclude that the transitions to 5 D account for the change and that 5 D is much more readily ionized than the 4 P states.

[5] Ruark and Urey, Atoms, Molecules, and Quanta; McGraw Hill Co.
[6] Boeckner, B. S. Jour. Research, 5 (RP184), p. 13; July, 1930.

For all other cases we have no direct evidence as to the transitions involved. It seems reasonable to assume that other excited states are also changed to neighboring states by helium collisions. Since collisions with hydrogen and nitrogen reduce the probability to nearly zero, we conclude that most collisions in these gases give a nearly complete dissipation of energy. It is interesting to note that experiments on collision effects with excited mercury in the 2 $^3P_1$ state show that hydrogen and oxygen reduce the atom to the normal state, while for nitrogen, as well as for the noble gases, the predominant effect is the minimum energy change from 2 $^3P_1$ to 2 ^3P_o.

Numerical values of $\sigma^2\tau'$ and of E_f/E_o are given in Table 4 for every case where experimental data justified a numerical estimate. They are computed from the slopes and intercepts of the straight lines given by reciprocal plots in accordance with equations (2) and (6). We include for comparison values of $\sigma^2\tau$ for cæsium-cæsium collisions. $\sigma^2\tau'$ for 5 P and 6 P remains of the same magnitude for all foreign gases except for the questionable value of argon. The observed differences in effectiveness at the same pressure are accounted for by the change in A in equation (6). These values are all of the order of 1 per cent of $\sigma^2\tau$ for cæsium-cæsium collisions. In the earlier paper we have estimated that for 5 P, τ is less than 10^{-5} and more than 10^{-6} which leads to a value of the collision radius between 10^{-7} and 3×10^{-7} for cæsium-cæsium collisions. For foreign gases, τ' is roughly ½ τ and σ between 1.4 and 4×10^{-8} for 5 P. The radius for collisions with foreign gases agrees in magnitude with ordinary atomic dimensions; the radius for cæsium-cæsium collisions is abnormal. The results show that the large radii are not determined by the electron charge distribution in states of high quantum number, for they are not characteristic of the state of excitation.

TABLE 4.—*Constants for collisions of excited cæsium with gases*

Line	Cs-Cs	Cs-N_2		Cs-He		Cs-H_2		Cs-A	
	$\sigma^2\tau$	$\sigma^2\tau'$	E_f/E_o	$\sigma^2\tau'$	E_f/E_o	$\sigma^2\tau'$	E_f/E_o	$\sigma^2\tau'$	E_f/E_o
3888	0.22×10^{-19}	1.10×10^{-21}	0.18	0.067×10^{-21}	1.7	1.0×10^{-21}	0	----------	>1
3877				.013	3.0				
3612	1.0	.93	.04	1.07	.74	1.0	0	0.07×10^{-21}	0
3477	1.1	1.25	.12	.38	.56	1.0	0	$.07\times10^{-21}$	0
3398	1.1	.83	.12	.50	.69	.45	0	$.04\times10^{-21}$	0
3349	1.0	.51	.12	.16	.80	.25	0	----------	--------
3280	2.0	.76	.38	----------	--------	----------	--------	----------	--------
3240	6.0	3.5	.72	----------	--------	----------	--------	----------	--------

Table 5 gives values of $\sigma^2\,\tau'$ for nitrogen at various cæsium pressures based on a single observed point at 0.134 mm of nitrogen and a value of the intercept taken from Figure 2. The change in $\sigma^2\,\tau'$ according to the simple theory given in the introduction depends on the change in τ' with vapor pressure, for σ should remain constant. We include in Table 5 computed values based on the variation of τ' as given by equation (5). There is a qualitative agreement, though the accidental variations are large.

TABLE 5.—*Effect of nitrogen at various cæsium pressures*

Cs pressure	Theoretical change	$\sigma^2\tau' \times 10^{21}$				
		3,612	3,477	3,398	3,349	3,280
0.0126	1.0	0.89	0.76	0.57	0.37	0.16
.0048	1.9	.93	1.25	.83	.51	.76
.0028	2.5	2.1	2.2	2.4	1.4	1.9
.0019	2.9	2.3	3.5	2.2	1.5	3.3

This rough agreement is of some significance in connection with collision processes in pure cæsium vapor. The derivation of the variation in actual life resulting from collisions with cæsium atoms rests on the assumption that in a collision the excited state is destroyed whether or not ionization is produced. This assumption was introduced largely for simplicity. If excited states are destroyed only in the event of ionization, then the actual life will be modified much less than is predicted by equation (5). Observed variations are, if anything, greater than the predicted change. Support for the conclusion that excited states are destroyed at collision is found in the observation by Boeckner that the resonance radiation excited by 3,888 becomes very faint when the cæsium pressure is increased above a few thousandths and surface resonance was not observed at higher pressures.

In the earlier paper we give a picture of the ionization process which implies that some, if not all, of the collisions that fail to give ionization give band emission spectra. It will be of interest to look for a molecular emission spectrum excited by atomic absorption under conditions of moderately high pressure.

At the highest pressure given in Table 5 (0.012 mm) the value of τ' is about one-fifth of the radiation life for states 5 P to 8 P; and, to a first approximation, we can neglect τ in the relation $\frac{1}{\tau'}=\frac{1}{\tau}+\frac{1}{T}$ and assume that $\tau'=T$. Since T is proportional to $1/\sigma^2$ for cæsium-cæsium collisions, $\tau'\sigma^2$ (nitrogen) is proportional to the ratio of σ^2 for nitrogen to σ^2 for cæsium. The decrease in $\sigma^2\tau'$ as we go to higher states indicates a decrease in the ratio of collision areas for the two kinds of collisions. The collision areas for cæsium-cæsium collisions presumably decrease with increasing quantum number between 5 P and 10 P and the collision areas for cæsium-nitrogen collisions decrease much faster.

The magnitude of the collision area might be expected to depend on whether or not chemical combination can take place. At least this is indicated in experiments by Lunn and Bichowsky [7] on the scattering of atomic hydrogen by foreign gases. The excited cæsium-cæsium collision involves a chemical reaction according to our viewpoint, and the large collision area is to be expected.

We might expect that the nearly complete quenching given by both H_2 and N_2 results from a transfer of the excitation energy of the cæsium atom into vibration energy of the molecules. All the m P levels fall in the range of discrete vibration states for both molecules. This suggests that, where the energy difference between an excited

[7] Preliminary note, Phys. Rev., 35, p. 563; 1930.

state and a vibrational level happens to be small, the value of σ will be abnormally large. There is no evidence of any such effect and both gases give values of σ much like helium.

The theory, as presented in the introduction and in the earlier paper, gives an ideally simplified picture of the complicated processes that are to be expected when an atom in a state of high quantum number collides with another atom. There are many possible transitions, and each will have a characteristic collision radius and efficiency. The observed effect is presumably a sort of average of these different primary effects. Again, there are many secondary effects, such as reabsorption of resonance radiation and successive collisions either reversing or increasing the effect of the first collision. These will, in general, give a curvature to the reciprocal plots and the procedure of drawing a straight line through observed points, which are too inaccurate to show a curvature, may involve a large systematic error. Detailed analyses of the results on quenching of resonance radiation in mercury vapor have shown that these secondary effects are by no means negligible.[8] [9]

The important feature of this work is that for the first time it has been possible to obtain approximate values of $\sigma^2\tau$ for a series of excited states in various gases with some qualitative evidence as to the effects produced at collision.

WASHINGTON, April 15, 1930.

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[8] Foote, Phys. Rev., **30**, p. 288; 1927.
[9] Gaviola, Phys. Rev., **33**, p. 309; 1929.